

IV. "On Certain Properties of Metals considered in Relation to the Periodic Law." By W. C. ROBERTS-AUSTEN, C.B., F.R.S. Received March 12, 1891.

In a previous paper published in the 'Philosophical Transactions' (1888, A, pp. 339—349), the effect of about 0·2 per cent. of impurities on the mechanical properties of gold was examined, the results of the experiments showing that metals which diminish its tenacity and extensibility have high atomic volumes, while those which increase these properties have either the same atomic volume as gold or a lower one. The behaviour of aluminium and of lithium appeared to be somewhat exceptional. Gold contaminated with 0·2 per cent. of aluminium should, if the theory set forth in the paper be correct, have a tensile strength of about 7 tons per square inch; but it was found to be capable of sustaining a load of nearly 9 tons per square inch without breaking. It became necessary, therefore, to ascertain whether the cooling of a mass of gold containing aluminium presents any peculiarities, more especially as Osmond's* recent work leads to the conclusion that a pure metal can exist in two distinct molecular forms, and that the passage of the ordinary modification of a metal to the allotropic one may either be hastened or retarded by the presence of impurity.

In order to continue the investigation, a trustworthy pyrometer was needed, and this has fortunately been provided by the thermoelectric junction of platinum, and platinum with 10 per cent. of rhodium, the use of which was suggested by M. Le Chatelier.† It appears to be superior to any other of the thermo-junctions which have previously been used, and some experiments made in 1889 satisfied me that the appliance is an extremely delicate and useful one for temperatures between 500° and 1100° C. In a recent report to the Institution of Mechanical Engineers, in which details of the method of calibration are embodied, I have described a suitable arrangement for obtaining, by the aid of photography, autographic curves which represent the cooling or heating of masses of metal.

It consists in enclosing a galvanometer of the Déprez and d'Arsonval type in a large camera; a fixed mirror, F, being placed below the movable mirror, M, of the galvanometer, so that the light from the lime cylinder, L, reflected in the mirror H, passes to both mirrors, F and M, and is reflected in the direction of a fine hori-

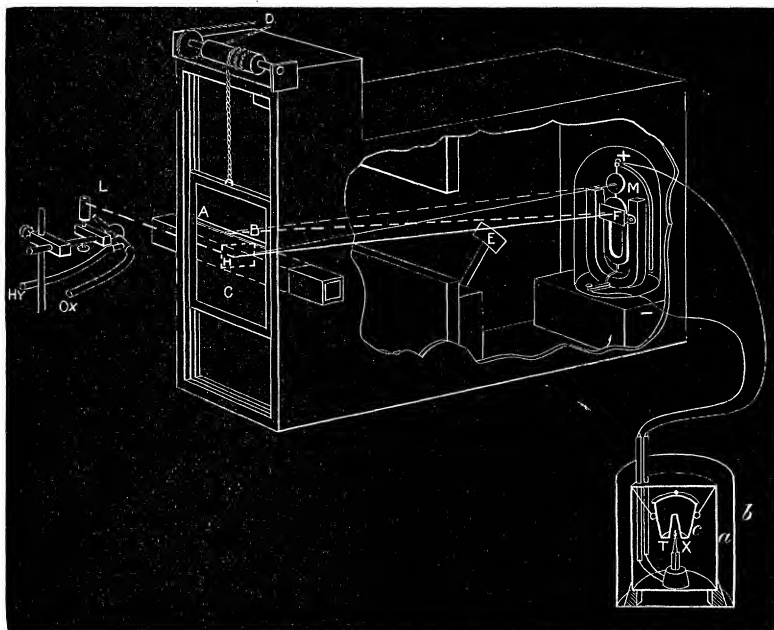
* 'Comptes Rendus,' vol. 110, 1890, p. 346. 'Journ. Iron and Steel Inst.,' 1890, Part 7, p. 38.

† 'Bull. Soc. Chim., Paris,' vol. 47, 1887, p. 2. 'Journal de Physique,' vol. 6, 1887, p. 23.

zontal slit, AB, behind which a sensitised photographic plate, C, is drawn vertically, past the slit, by means of gearing, D, driven by clockwork. The ray from the fixed mirror is interrupted periodically by the vane, E, and a beaded datum line is given which enables any irregularity in the advance of the plate to be detected.

The amount of divergence from its datum line of the spot of light reflected by the movable mirror at any given moment bears a relation (which can readily be found by calibration) to the temperature to which the thermo-junction X is heated, and variations of temperature are recorded by a curve which is the resultant of the upward movement of the plate and the horizontal movement of the spot of light. The complete arrangement is shown in the diagram fig. 1.

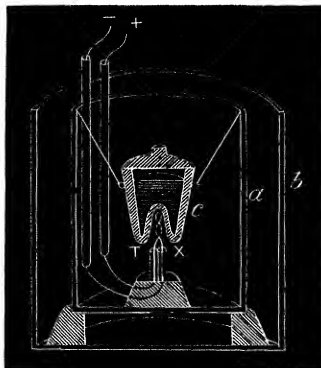
FIG. 1.



The portion of the arrangement in which the thermo-junction is placed is also shown in fig. 2, which is drawn on a larger scale than fig. 1, the same letters being used in both.

The thermo-junction X is inserted in a tubulure, T, of a specially constructed crucible of plumbago, c, which contains about 5 oz. of pure molten gold, and is allowed to cool down slowly inside a vessel, a, of silver 105 mm. diameter, and polished internally. The cylinder, b, is of tin plate, polished internally and blackened outside.

FIG. 2.



A photographic record of the cooling of pure gold is represented by the thicker of the dotted lines in fig. 3. The mass of gold had in this case an initial temperature of about 1250° C., which fell to 1045° C. when the mass began to solidify. The curve is approximately horizontal during solidification, and throughout its entire course appears to be a perfectly normal curve of a cooling mass of metal, no points of exceptional absorption or evolution of heat, such as would occur in iron, being observable.

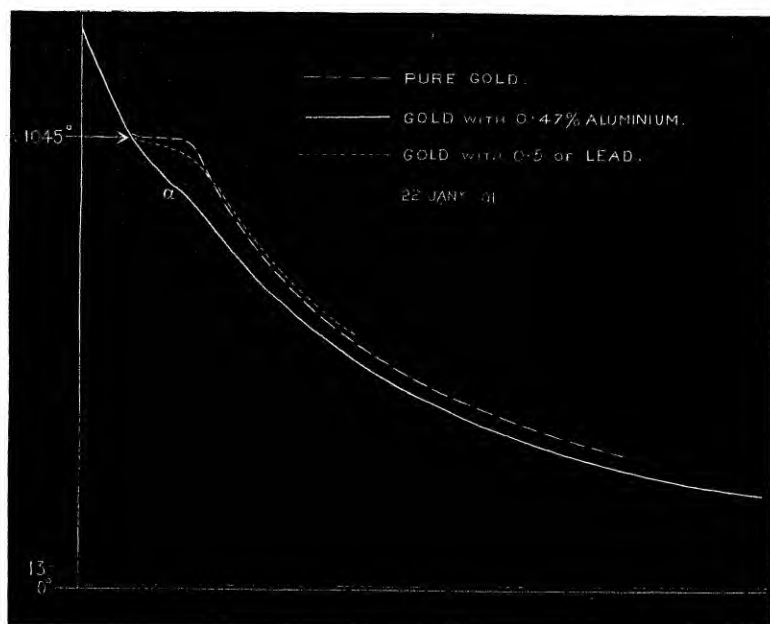
A curve obtained in a similar way, and representing the cooling of gold with 0.5 per cent. of lead, is shown by the thin dotted line in the same figure. It is similar to the one representing the cooling of pure gold, but it will be evident that the presence of lead lowers the freezing point of gold by an amount which is found by measurement to be about $7^{\circ}.5$ C.

A very different molecular condition is, however, established by the presence of aluminium. With 0.47 per cent. of this element the true freezing point can be detected, but is nearly obliterated (fig. 3), and the mass does not become truly solid until the point marked *a* is reached when the temperature has fallen to 900° C.

It is of interest to ascertain how far the lowering of the freezing point of gold is in accordance with the results of Raoult's investigations on the lowering of the freezing point of solutions. His generalisations have been tested in the case of solutions of metals in metals with low melting points (tin, lead, and bismuth), in an admirable series of experiments by Heycock and Neville.* In order to calculate the lowering of the freezing point of gold produced by one atom of the added element to 100 atoms of the solvent, which has been the usual method of stating such results, it is necessary to know the latent

* 'Journ. Chem. Soc.,' vol. 55, 1889, p. 666; vol. 57, 1890, pp. 376 and 656.

FIG. 3.



heat of fusion of gold, and this had not been determined, probably because the accurate measurement of the latent and specific heats of metals with high melting points, such as gold, presents many more difficulties than the determinations of similar constants for bodies having low melting points.

Violle* found the specific heat of platinum at different temperatures by heating a piece of the metal in a specially constructed muffle, the temperature being simultaneously determined by means of a porcelain air-thermometer. The temperature of the metal being known, he plunged it into a calorimeter, and calculated from the data he obtained the mean specific heat of platinum between the extreme temperatures of the experiment. By making many experiments at different temperatures, he was able to deduce the specific heat of platinum at any point within the range, and he found that it regularly increased with the temperature. The data, thus afforded, enabled him to obtain the freezing point of platinum by transferring metal just *after* solidification into the calorimeter. Further, by pouring metal just *before* its solidification into water, it was easy to determine the total amount of heat evolved during cooling. Hence, knowing

* 'Comptes Rendus,' vol. 85, 1877, pp. 543—546.

the amount of heat evolved by the mass after it had become solid, and deducting this amount from the total heat transferred to the water by the melted platinum, he obtained the latent heat of fusion of the metal.

He also determined* the specific heat and melting point (1045° C.) in the case of gold, but he does not appear to have ascertained what is the latent heat of fusion of the precious metal. The following experiments were therefore made, in order to afford a basis for calculating the theoretical lowering of the freezing point of gold which a given addition of impurity should produce.

A calorimeter of polished silver, 10.5 cm. diameter, and 15.5 cm. high, was supported upon three points of cork within a bright metallic vessel, blackened externally, and constituting an air-jacket. The amount of water employed varied from 800 to 1088 grams. The stirrer was a thin sheet of mica, mounted upon a silver wire, bent at its lower end into the form of a hoop; the mica also served to catch the gold poured into the water. In experiments E to I, the stirring was effected by silver vanes, of a form suggested by Professor Rücker, actuated by a small electromotor. Quantities of very pure gold, varying from 68 to 123 grams, were melted in a small clay crucible and poured into the calorimeter.

This portion of the manipulation was performed by my assistant, Mr. Groves, whose long experience in melting gold enabled him to select the latest moment before solidification at which the gold could be poured. In Experiments A and B and E to I, the temperature of the molten mass was measured, by the aid of the thermo-junction previously described, which was placed directly in the molten gold, up to the moment of pouring, and it is believed that the temperature of the mass was known to within 10° C.

At the end of each experiment, the gold poured into the calorimeter was carefully collected and weighed. The thermometer used was a very sensitive one with fixed zero, and made by Hicks, of Hatton Garden; it could easily be read to $0^{\circ}.02$ C. The depth of water employed was sufficient to prevent the evolution of steam, and none was observed to escape in any of the experiments recorded.

The calculations are as follows:—

Let P = weight of water in calorimeter.

p_1c_1 = water equivalent of calorimeter.

p_2c_2 = „ „ thermometer.

p = weight of gold employed.

c = average specific heat of gold (Violle).

t = initial temperature of the molten gold.

T = „ „ water.

t_1 = final temperature of the water.

* ‘Comptes Rendus,’ vol. 89, 1879, pp. 702–703; 92, 1881, pp. 886–8.

The total quantity of heat carried to the calorimeter by p grams of gold consists of the amount of heat which was required to raise the temperature of the metal to its melting point, *plus* the amount actually required to melt it; or

$$(P + p_1c_1 + p_2c_2)(t_1 - T) = pc(t - t_1) + p\lambda,$$

where λ is the latent heat of fusion of gold required;

$$\therefore \lambda = \frac{(P + p_1c_1 + p_2c_2)(t_1 - T) - pc(t - t_1)}{p}.$$

Taking, therefore, 16.3 as the latent heat of fusion of gold, and proceeding to find the lowering $\delta\theta$ of the freezing point, due to the presence of an impurity,

$$\delta\theta = \frac{\theta\omega}{\lambda\rho},$$

where

θ = freezing point of gold, from absolute zero,

ω = osmotic pressure in dynes,

ρ = density of the solvent,

λ = latent heat of fusion of the solvent in dynes.

Inserting values

$$\begin{aligned} \delta\theta &= \frac{\frac{1040 + 273}{1} \times \frac{(1013 \times 10^3 \times 22.3 \times 1300)}{19.6 \times 273}}{\rho \times 16.3 \times 41.6 \times 10^6} \\ &= \frac{1313 \times 1013 \times 22.3 \times 1300}{19.6 \times 16.3 \times 41.6 \times 10^3 \times 273} \\ &= 10.6 \text{ C.} \end{aligned}$$

Experiments are in progress with a view to ascertain whether the mean specific heat of very pure gold is the same as that found by Violle, for there is every reason to believe that the presence of impurity has great influence upon this constant. A few measurements already made would seem to indicate that his result is low, and this is important, because a slight difference in the specific heat will have a material effect upon the latent heat of fusion, and consequently on the theoretical atomic fall in the freezing point produced by aluminium. In order to ascertain whether aluminium would give the normal lowering of the freezing point (10.6 for each atom present in 100 atoms of gold) a crucible, fitted with a tubulure, as already described, was taken, and 130 grams of very pure gold was melted in it. The crucible was then placed over the thermo-junction, and allowed to cool, the freezing point of the metal it contained

Table of Experiments. In Centigrade-gramme Units.

	P.	p_1c_1 .	p_2c_2 .	p .	c .	t .	T.	t_1 .	λ .	Remarks.
A ...	800.75	15.42	0.86	84.72	0.0352	1075*	13° 4	19° 0	16.83	Solidification had just begun.
B ...	800.75	15.42	0.86	68.68		1050*	12.9	17.4	17.07	
C....	983.1	15.72	1.16	87.11		1045	9.68	14.52	16.51	
D ...	808.7	15.72	1.16	76.05		1045	10.34	15.18	16.29	
E ...	1088.6	16.37	1.16	119.6		1045*	11.79	17.47	16.36	
F....	1088.6	16.37	1.16	123.0		1045*	11.74	17.50	15.62	
G ...	1088.6	16.37	1.16	79.19		1045*	12.11	15.88	16.43	
H ...	1088.6	16.37	1.16	105.05		1085*	13.52	18.61	16.05	
I....	1088.6	16.37	1.16	102.75		1070*	14.30	19.21	15.87	

* These temperatures were measured by the aid of the pyrometer, and, as the metal was slightly above its melting point, it was necessary to assume that the specific heat of the fluid gold is practically the same as that of solid gold near its melting point. The slope of the autographic curves, moreover, shows that any error so introduced would be but small. [April 20, 1891.—Experiments E to I have been added since the paper was read.]

being recorded in the usual way by a curve. The gold was then re-melted, and a weighed quantity of aluminium added, the mass being stirred and the temperature of its freezing point measured and recorded in a curve.

The addition of 0·2 per cent. of aluminium produced an appreciable fall in the freezing point, but this initial fall is only indicated by a change in direction of the curve. The fall as measured upon the photographic plate is only 1 mm., which nevertheless corresponds to a difference of temperature of 7°·68 C.

A further addition of 0·2 per cent. of aluminium (making 0·4 per cent.) increased the fall to 1·8 mm., corresponding to 14°·28 C. It may be urged that these measurements are small, but the observations were repeated with a scale some distance from the galvanometer, and chronographic records gave results having the same values.

An experiment with gold in which 1 per cent. of aluminium was present also confirms this; the fall in temperature of the freezing point was in this case 33°·66 C., but there were indications that the gold, the solvent, was becoming saturated.

Now 0·2 per cent. of aluminium corresponds to $2/10 \times 196/27\cdot5 = 1\cdot42$ atom per 100 atoms of gold.*

Hence the fall per atom present per hundred atoms of gold = $7\cdot68/1\cdot42 = 5\cdot4$ C.

Similarly, a percentage of 0·4 corresponds to $4/10 \times 196/27\cdot5 = 2\cdot85$ atoms per hundred of gold, and the fall per atom = $14\cdot28/2\cdot85 = 5\cdot0$ C.

With 1 per cent. of aluminium the total fall will be due to 7·16 atoms per hundred of gold; hence the atomic fall will be $33\cdot66/7\cdot16 = 4\cdot7$ C.

It may be added that experiments (as yet incomplete) seem to show that lead, bismuth, silicon, and platinum cause a much greater "atomic fall" in the freezing point of gold than aluminium does.

The relations of aluminium to gold would, therefore, appear to be peculiar in more ways than one. The curve (fig. 3) clearly indicates that aluminium has a remarkable influence on the cooling of a mass of gold, and in view of this it would seem strange that calculations based on the atomic weight of aluminium should show that it delays the *initial* solidification of gold less than other elements. The *complete* solidification is, however, much retarded; for merely stirring a mass of gold contaminated with very little aluminium reveals the fact that the added element has set up during the solidification of the mass a "pasty stage" which continues through an unusually long range of temperature.

In the metallurgy of iron, aluminium is known to play an im-

* 196 is the atomic weight of gold, 27·5 that of aluminium.

portant part, and the introduction of a small quantity of it renders it possible to cast very mild steel or even "wrought" iron into forms which are remarkable for delicacy and soundness. The mode of action of the aluminium on iron in the "mitis castings" has given rise to wide divergence of opinion, but the view that it acts by the removal of oxide, or of occluded oxygen, has gained much favour. In the case of gold, which has neither occluded oxygen nor oxide to lose, the castings of the metal with 0·2 per cent. of aluminium are also remarkably sound, and, as experiments prove, very tenacious; the action of the aluminium is, therefore, probably a molecular one of much complexity.

It may be pointed out that the presence in gold of quantities of silver which vary from 0·1 to 4·0 per cent. does not lower the freezing point of the mass. Messrs. Heycock and Neville, who witnessed certain of the experiments above described, inform me of the hitherto unpublished fact, observed by them, that the presence of thallium does not lower the freezing point of lead.

The close concordance in both these cases between the atomic volumes of the mass of metal and the added impurity is of special interest in connexion with the generalisation given in my earlier paper and re-stated on the first page of this. Silver has the same atomic volume as gold, and if present in small quantity, produces no effect on either its tenacity or its freezing point.

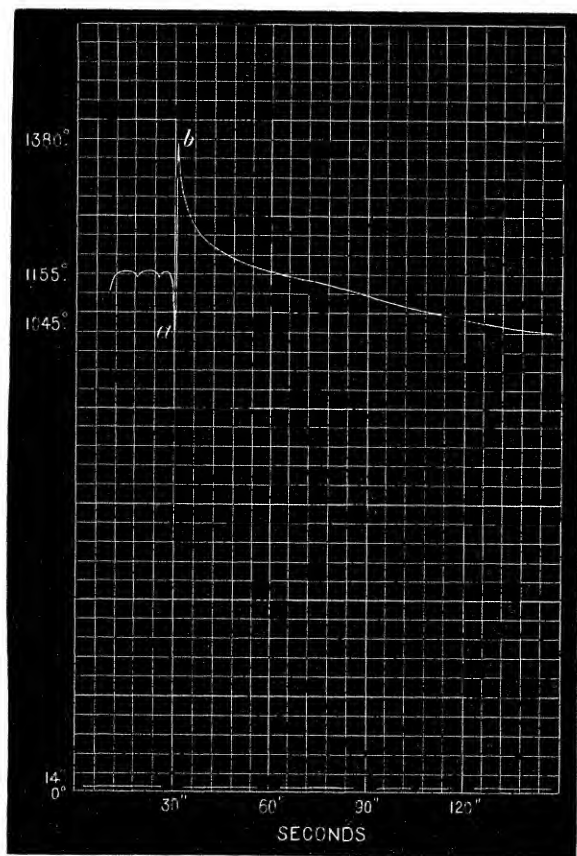
Throughout these experiments gold has simply been employed for the sake of its freedom from liability to oxidation, but other metals must be studied, and it is worthy of record that Hadfield has recently shown that the parts played by aluminium and by silicon in steel are almost identical. Most of the physical properties of aluminium and silicon, in a free state, are totally different, but they possess the same atomic volume, and when they are alloyed with iron they affect it in precisely the same way.

I have to express my thanks to my assistant, Mr. H. C. Jenkins, for his aid in conducting these experiments.

[April 20, 1891.—In the course of the investigation, it became evident that, as is the case when aluminium is alloyed with copper or iron, the addition of aluminium to gold is attended with evolution of heat. The following experiment was therefore arranged, with a view to obtain evidence on this point:—

A mass of 30 grams of gold, contained in an unglazed porcelain crucible, was placed in the centre of a block of firebrick and strongly heated up to well above the melting point of the metal. The thermojunction was inserted directly in the gold, and the spot of light from the galvanometer allowed to fall in the usual way on to the sensitised plate (fig. 1). A piece of cold aluminium, equal in weight to 1 per cent. of the mass of gold, was then added and rapidly stirred. The

FIG. 4.



autographic curve, from which fig. 4 was plotted, showed that the first effect of the added aluminium is, as might be expected, to lower the temperature of the gold to a point *a* which proved to be close to its solidifying point, 1045°; the temperature instantly rises, however, to a point *b*, which is 225° higher than the initial temperature of the gold. The experiment is not strictly quantitative, as the perfect admixture of the aluminium could not be ensured; but it is probable that true combination of aluminium and gold has taken place, which would doubtless greatly affect the physical constants of the mass.]

Fall

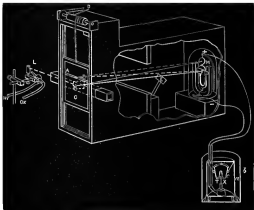


FIG. 3.



FIG. 8.

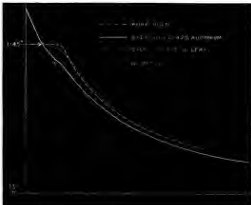


FIG. 4.

